PATENT SPECIFICATION

Application Date: May 26, 1943. No. 8386/43. 565,951

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Complete Specification Accepted: Dec. 6, 1944.

PROVISIONAL SPECIFICATION

New Monoazo Pigments

We, E. I. Du Pont de Nemours and Co., of Wilmington, Delaware, United States of America, a corporation organised and existing under the laws of the State of Delaware, United States of America, and Donovan Erb Kvalnes, of 10, Ziegler Tract, Pennsgrove, New Jersey, and Harold Edward Woodward, of Bay Street, Fenwick Park, Pennsgrove, New Jersey, United States of America, both citizens of the United States of America, do hereby declare the nature of this invention to be as follows:—

This invention relates to new monoazo pigments and especially to certain metal complexes of monoazo compounds in which the coupling component is 2-hydroxy-3-naphthoic acid or a derivative thereof.

The objects of the invention are attained in general by coupling with 2-hydroxy-3-naphthoic acid a diazotized aryl-amine which is devoid of hydroxy groups ortho to the sole diazotisable amino group and which is devoid of carboxy groups and sulphonic acid groups, and then form a nickeliferous or cobaltiferous metal complex which contains two metal atoms per two molecules of the monoazo combination, at least one of the metal atoms being nickel or cobalt and the other metal atoms being from a group consisting of metals having an atomic weight of 54 to 65, and the alkaline earth metals, such as copper, nickel, cobalt, iron, manganese, calcium, barium and strontium.

The coupling component, 2-hydroxy-3-naphthoic acid, may be substituted on the ring not containing the hydroxy group with halogen, nitro, alkyl or alkoxy groups. Examples of such substituted coupling components are 6-chloro-, 6-bromo-, 5-nitro-, 8-nitro-, 6-methyl-, 6-ethoxy- and 6-methoxy-2-hydroxy-3-naphthoic acid.

The components of the present invention are useful pigments which range in shade through yellows, reds, blues and browns and are of excellent light-fastness. The new pigments may be used for colouring inks, paints, textile printing emulsions, bases and similar compositions.

[*Price* 1/-]

The invention will be more fully set forth in the following more detailed description which includes examples that are given as illustrative embodiments of the invention and not as limitations thereof. Parts are expressed in parts by weight unless otherwise noted.

Example 1.

Para-nitro-aniline (138 parts) was diazotised with 91 parts of hydrochloric acid (100%) and 69 parts of sodium nitrite. The solution of the diazonium chloride was added to an alkaline solution containing 200 parts of 2-hydroxy-3-naphthoic acid, 42 parts of sodium hydroxide and 159 parts of sodium carbonate, in 4000 parts of water, the temperature being kept at 10° C. during the coupling. After the coupling was complete, the insoluble monoazo was filtered and washed. It was then stirred into 4000 parts of water. To this slurry was added a solution consisting of 262 parts of nickel chloride ($NiCl_2.6H_2O$) in 500 parts of water to which had been added 500 parts of concentrated ammonium hydroxide. The suspension was heated to 90° C. and held at this temperature for 3 hours. It was then filtered and the resulting pigment was washed.

Analysis of the product showed that it contained one atom of nickel to two atoms of nitrogen, exclusive of ammoniacal nitrogen and the nitrogen of the nitro group. It contained 1/2 molecule of co-ordinated ammonia.

Example 2.

The pigment of Example 1 was made by a modified process in which the monoazo coupling was made in acid solution by using 200 parts of sodium acetate as buffer in place of 159 parts of sodium carbonate. The metallisation was modified in that it was carried out in the presence of 40 parts of 50% para soap which was added before the solution of nickel ammonium chloride was added. The pigment had the same chemical analysis as that obtained in Example 1, but it gave a much bluer colour when printed on cotton from a lacquer emulsion, and in inks it gave a darker mass tone and a bluer tint.

The same pigment was made by the

same process except that about two molecular equivalents of sodium hydroxide were used as the acid acceptor instead of ammonia. The sodium hydroxide in dilute water solution was gradually added to the metallisation medium as the metallisation proceeded and at a rate such that the medium had a pH value of 6.8 to 7.0.

EXAMPLE 3.

By using an equal weight of cobaltous chloride ($CoCl_2.6H_2O$) in place of the $NiCl_2.6H_2O$ in Example 1, a pigment was obtained which was somewhat duller and less fast to light than the pigment of Example 1. When hydrogen peroxide was added to the metallising medium, in order to form a cobaltic compound, the resulting pigment was browner and slightly better in light fastness.

EXAMPLE 4.

By using meta-nitro-aniline in place of para-nitro-aniline in Example 1, a pigment was obtained which gave reddish shades of brown when used in printing lacquers or printing inks. The fastness properties were very good.

EXAMPLE 5.

A pigment was made as described in Example 1 except that 119 parts of $NiCl_2.6H_2O$ and 122 parts of $BaCl_2.2H_2O$ were used in place of 262 parts of $NiCl_2.6H_2O$. The pigment obtained was similar in shade and fastness to light. The pigment obtained from a mixture of equivalent parts of nickel and cobalt was also a maroon of good light fastness. When a mixture of equivalent parts of nickel chloride and manganese sulphate was used, the pigment obtained was yellower but the light fastness was also good.

EXAMPLE 6.

The monoza colour made by coupling the diazo of 162 parts of 2:5-dichloraniline with 200 parts of 2-hydroxy-3-naphthoic acid, as in Example 1, was slurried in water. A water solution containing 60 parts of $CaCl_2$ was added to the slurry, followed by a solution of 119 parts of $NiCl_2.6H_2O$ in 300 parts water and 600 parts strong ammonium hydroxide solution. The slurry was heated to 90° C., held at this temperature for about two hours and filtered. The dried pigment, rubbed in lithographic varnish, gave a dark red ink, non-bleeding in oil, and of good light fastness.

EXAMPLE 7.

Aniline (93 parts) was diazotised with 300 parts of ice and 250 parts of 10 Normal hydrochloric acid and 200 parts of 5 Normal sodium nitrite. The solution of the diazonium chloride was added to an alkaline solution containing 200 parts of 2-hydroxy-3-naphthoic acid, 42 parts of sodium hydroxide and 159 parts of sodium carbonate in 4000 parts of water, the temperature being kept at 10° C. during the coupling. After the coupling was complete the insoluble monoazo compound was filtered and washed with 5% brine. It was then stirred into 4000 parts of water and heated to 90° C. To this slurry was added a solution composed of 262 parts of nickel chloride ($NiCl_2.6H_2O$) in 500 parts of water and 500 parts of concentrated ammonium hydroxide solution. The slurry was held at 90° C. for 3 hours. The pigment was then filtered and washed.

When this pigment was used for printing textiles, a red brown or dull red print was obtained of excellent light fastness and very good in other fastness tests.

This pigment was used for colouring paper both in the beater and in a wall paper coating. It gave dull red papers which were superior in light fastness to papers coloured with other red pigments that are commercially used for this purpose.

This pigment was also prepared by using other basic compounds than ammonia in the reaction with nickel chloride. For example, diethanolamine, triethanolamine, pyridine or morpholine are sufficiently basic so that a similar brown pigment was obtained.

EXAMPLE 8.

Alpha-naphthylamine (143 parts) was diazotised in the usual way with 250 parts of 10 Normal hydrochloric acid and 200 parts of 5 Normal sodium nitrite. The filtered solution was added to a solution composed of 200 parts of 2-hydroxy-3-naphthoic acid dissolved in 4000 parts of water containing 42 parts of sodium hydroxide and 159 parts of sodium carbonate. The insoluble monoazo colour was filtered and washed. The filter cake was slurried in 3000 parts water. To this suspension was added 262 parts of nickel chloride ($NiCl_2.6H_2O$) and 93 parts of aniline. The mixture was then heated to 90° C. and held at this temperature for 3 hours. The pigment was then filtered, washed and dried. The dried pigment was rubbed into a lithographic varnish, resulting in a black ink having a violet tint. The fastness to light was very good.

The same pigment was obtained by using in place of 93 parts of aniline, an equivalent molecular proportion of phenyl ethanolamine or phenyl diethanolamine or 120 parts urea or 500 parts of concentrated ammonium hydroxide as the acid acceptor.

The following table shows the results obtained by using other diazo components than para-nitro aniline, coupling with 2-hydroxy-3-naphthoic acid and then metal-

lising with the metal indicated and in the manner described in the foregoing examples. The properties of these pigments are similar to those heretofore described except where it is otherwise noted.

Example	Diazo Component	Metal	Colour of Textile Print
9	Aniline	Cobalt	Red Brown
10	para-Chlor-aniline	,,	,, ,,
11	,, ,, ,,	Nickel	,, ,,
12	meta- ,, ,,	,,	,, ,,
13	meta-Nitroaniline	Cobalt	,, ,,
14	3-Nitro-4-chlor-aniline	,,	,, ,,
15	,, ,, ,, ,, ,,	Nickel	,, ,,
16	2-Chlor-4-nitro-aniline	Cobalt	,, ,,
17	,, ,, ,, ,, ,,	Nickel	,, ,,
18	2-Nitro-4-amino-toluene	Cobalt	Brown
19	,, ,, ,, ,, ,,	Nickel	Red Brown
20	2-Amino-5-nitro-toluene	Cobalt	,, ,,
21	,, ,, ,, ,, ,,	Nickel	,, ,,
22	*o*-Anisidine	,,	Maroon
23	*p*-Anisidine	,,	Brown
24	2-Amino-4-nitro-anisole	Cobalt	Bordeaux
25	,, ,, ,, ,, ,,	Nickel	,, (redder)
26	2-Amino-5-nitro-anisole	Cobalt	,,
27	,, ,, ,, ,, ,,	Nickel	Violet
28	3-Chlor-4-ethoxy-aniline	Cobalt	Bordeaux
29	,, ,, ,, ,, ,,	Nickel	,,
30	4-Amino-4'-ethoxy-diphenylamine	Cobalt	Blue
31	,, ,, ,, ,, ,,	Nickel	,,
32	alpha-Naphthylamine	Cobalt	,,
33	beta-Naphthylamine	,,	Brown
34	,, ,,	Nickel	Bordeaux
35	alpha-Amino-anthraquinone	Cobalt	Red Brown
36	,, ,, ,,	Nickel	,, ,,

Example of other suitable diazo components are ortho-, meta-, para-toluidine; 1:3-dimethyl-4-aminobenzene and para-xylidine; ortho-chlor-aniline; ortho- meta- and para-bromo-aniline; chloro-toluidines; meta-anisidine; ortho-, meta- and para-phenetidines; chloro-anisidines, other chloro-phenetidines, 2:5-dimethoxy-aniline; other nitro-chlor-anilines; other nitro-anisidines; nitro-phenetidines; meta-amino-benzotrifluoride; other dichlor-anilines; trichlor-anilines; other nitro-toluidines; nitro-chlor-toluidines; benzoyl-meta- and para-phenylene-diamine; meta- and para-amino-acetophenone; meta- and para-amino-benzophenone; ortho-, meta- and para-amino-phenyl-alkyl sulphones; para-dodecyl-aniline; ortho-, meta- and para-amino-benzene-sulphon-dimethyl-amides; ortho-, meta-, and para-cyano-aniline; ortho-, meta- and para-amino alkyl benzoates; ortho-, meta- and para-amino-diphenyl-ether; 4-nitro-4'-amino-diphenyl-sulphide; 4-amino-diphenyl-amine; 4-amino-4'-ethoxy-diphenyl-amine; 2- and 4-amino-diphenyl; 2-amino-benzothiazol; 2-amino-6-ethoxy-benzothiazol; 2-amino-4-methyl-thiazol; 5-, 6- and 8-amino-quinoline; 1-phenyl-3-methyl-4-amino-5-chlorpyrazol.

The metallisation does not go to completion in the presence of free mineral acids. A sufficient amount of an alkaline compound must be available in the medium as an acid acceptor to combine with the free acid as it is liberated from the inorganic salt and as the metallisation proceeds. The pH value of the metallisation medium should be greater than about 6.5. The term "acid acceptor" in the specification and claims refers to an alkaline compound which is added to the metallisation medium to maintain a pH value greater than 6.5 and which will combine with the free mineral acid as it is liberated during metallisation. Any alkaline substance which functions in the manner indicated can be used instead of the acid acceptors heretofore specifically mentioned. Illustrations of such other compounds are propylamine, mono-, di- and tri-methylamine, ethylamine, formamide, acetamide, dimethyl formamide, hexylamine, cyclohexylamine, methyl glucamine, taurine, beta-dimethyl amino propanol sulphonic acid, toluidines, xyli-

dines, naphthylamines, diphenylamine, piperazine, dimethyl sulphanilic acid, melamine, pyrrole, indole, carbazole, hexamethyleneimine, hexamethylene tetramine, mono- and di-methyl glycine, dimethylol urea, sodium formate and sodium oxalate, potassium glycolate, potassium gluconate, potassium tartrate, sodium citrate, sodium maleate, sodium succinate and sodium chloracetate. Some of these basic compounds coordinate with the metal complex in the manner similar to that which ammonia coordinates with the compound described in Example 1. This coordination depends to a large extent on the basic compound used and upon particular conditions present in the process of treatment.

In the metallising operation, the mixture is always alkaline, preferably having a pH value of about 7 to 10, and the salt of the metallising metal may be present in the molecular proportion which is needed as indicated by the formula given herein for the compounds, but a moderate excess, say about 10% of the salt over the amount indicated by theory, is desirable.

Dated the 26th day of May, 1943.

J. W. RIDSDALE,
Solicitor for the Applicants.

COMPLETE SPECIFICATION

New Monoazo Pigments

We, E. I. DU PONT DE NEMOURS AND Co., of Wilmington, Delaware, United States of America, a corporation organised and existing under the laws of the State of Delaware, United States of America, and DONOVAN ERB KVALNES, of 10, Ziegler Tract, Pennsgrove, New Jersey, and HAROLD EDWARD WOODWARD, of Bay Street, Fenwick Park, Pennsgrove, New Jersey, United States of America, both citizens of the United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to new monoazo pigments and especially to certain metal complexes of monoazo compounds in which the coupling component is 2-hydroxy-3-naphthoic acid or a derivative thereof.

The objects of the invention are attained in general by coupling with 2-hydroxy-3-naphthoic acid a diazotized aryl-amine which is devoid of hydroxy groups ortho to the sole diazotisable amino group and which is devoid of carboxy groups and sulphonic acid groups, and then treating with an agent yielding metal to form a nickeliferous or cobaltiferous metal complex which contains two metal atoms per two molecules of the monoazo combination, at least one of the metal atoms being nickel or cobalt and the other metal atoms being from a group consisting of metals having an atomic weight of 54 to 65, and the alkaline earth metals, such as copper, nickel, cobalt, iron, manganese, calcium, barium and strontium.

The coupling component, 2-hydroxy-3-naphthoic acid, may be substituted on the ring not containing the hydroxy group with halogen, nitro, alkyl or alkoxy groups. Examples of such substituted coupling components are 6-chloro- (made as described in German Specification No. 564,128), 6-bromo-, 5-nitro- and 8-nitro- (made as described in German Specification No. 611,284), 6-methyl-, (made as described in British Specification No. 391,987), 6-ethoxy- (made by a method analogous to that described for the 6-methoxy-compound in British Specification No. 366,140) and 6-methoxy-2-hydroxy-3-naphthoic acid.

The compounds of the present invention are useful pigments which range in shade through yellows, reds, blues and browns and are of excellent light-fastness. The new pigments may be used for colouring inks, paints, textile printing emulsions, paint extenders and similar compositions.

The invention will be more fully set forth in the following more detailed description which includes examples that are given as illustrative embodiments of the invention and not as limitations thereof. Parts are expressed in parts by weight unless otherwise noted.

EXAMPLE 1.

Para-nitro-aniline (138 parts) was diazotised with 91 parts of hydrochloric acid (100%) and 69 parts of sodium nitrite. The solution of the diazonium chloride was added to an alkaline solution containing 200 parts of 2-hydroxy-3-naphthoic acid, 42 parts of sodium hydroxide and 159 parts of sodium carbonate in 4000 parts of water, the temperature being kept at 10° C. during the coupling. After the coupling was complete, the insoluble monoazo compound was filtered and washed. It was then stirred into 4000 parts of water. To this slurry was added a solution consisting of 262 parts of nickel chloride ($NiCl_2.6H_2O$) in 500 parts

of water to which had been added 500 parts of aqueous ammonium hydroxide of sp. gr. 0.880. The suspension was heated to 90° C. and held at this temperature for 3 hours. It was then filtered and the resulting maroon pigment of good light fastness was washed.

Analysis of the product showed that it contained one atom of nickel to two atoms of nitrogen, exclusive of ammoniacal nitrogen and the nitrogen of the nitro group. It contained 1/2 molecule of co-ordinated ammonia.

EXAMPLE 2.

The pigment of Example 1 was made by a modified process in which the monoazo coupling was made in acid solution by using 200 parts of sodium acetate as buffer in place of 159 parts of sodium carbonate. The metallisation was modified in that it was carried out in the presence of 40 parts of 50% para soap which was added before the solution of nickel ammonium chloride was added. The pigment had the same chemical analysis as that obtained in Example 1, but it gave a much bluer colour when printed on cotton from a lacquer emulsion, and in inks it gave a darker mass tone and a bluer tint.

The same pigment was made by the same process except that about two molecular equivalents of sodium hydroxide were used as the acid acceptor instead of ammonia. The sodium hydroxide in dilute water solution was gradually added to the metallisation medium as the metallisation proceeded and at a rate such that the medium had a pH value of 6.8 to 7.0.

EXAMPLE 3.

By using an equal weight of cobaltous chloride ($CoCl_2.6H_2O$) in place of the $NiCl_2.6H_2O$ in Example 1, a pigment was obtained which was somewhat duller and less fast to light than the pigment of Example 1. When hydrogen peroxide was added to the metallising medium, in order to form a cobaltic compound, the resulting pigment was browner and slightly better in light fastness.

EXAMPLE 4.

By using meta-nitro-aniline in place of para-nitro-aniline in Example 1, a pigment was obtained which gave reddish shades of brown when used in printing lacquers or printing inks. The fastness properties were very good.

EXAMPLE 5.

A pigment was made as described in Example 1 except that 119 parts of $NiCl_2.6H_2O$ and 122 parts of $BaCl_2.2H_2O$ were used in place of 262 parts of $NiCl_2.6H_2O$. The pigment obtained was similar in shade and fastness to light. The pigment obtained from a mixture of equivalent parts of nickel and cobalt was also a maroon of good light fasteness. When a mixture of equivalent parts of nickel chloride and manganese sulphate was used, the pigment obtained was yellower but the light fastness was also good.

EXAMPLE 6.

The monoazo colour made by coupling the diazonium chloride from 162 parts of 2:5-dichloraniline with 200 parts of 2-hydroxy-3-naphthoic acid, as in Example 1, was slurried in water. A water solution containing 60 parts of $CaCl_2$ was added to the slurry, followed by a solution of 119 parts of $NiCl_2.6H_2O$ in 300 parts of water and 600 parts of aqueous ammonium hydroxide solution of sp. gr. 0.880. The slurry was heated to 90° C., held at this temperature about two hours and filtered. The dried pigment, rubbed in lithographic varnish, gave a dark red ink, non-bleeding in oil, and of good light fastness.

EXAMPLE 7.

Aniline (93 parts) was diazotised with 300 parts of ice and 250 parts of 10 Normal hydrochloric acid and 200 parts of 5 Normal sodium nitrite. The solution of the diazonium chloride was added to an alkaline solution containing 200 parts of 2-hydroxy-3-naphthoic acid, 42 parts of sodium hydroxide and 159 parts of sodium carbonate in 4000 parts of water, the temperature being kept at 10° C. during the coupling. After the coupling was complete the insoluble monoazo compound was filtred and washed with 5% brine. It was then stirred into 4000 parts of water and heated to 90° C. To this slurry was added a solution composed of 262 parts of nickel chloride ($NiCl_2.6H_2O$) in 500 parts of water and 500 parts of aqueous ammonium hydroxide solution of sp. gr. 0.880. The slurry was held at 90° C. for 3 hours. The pigment was then filtered and washed.

When this pigment was used for printing textiles, a red brown or dull red pigment was obtained of excellent light fastness and very good in other fastness tests.

This pigment was used for colouring paper both in the beater and in a wall paper coating. It gave dull red papers which were superior in light fastness to papers coloured with other red pigments that are commercially used for this purpose.

This pigment was also prepared by using other basic compounds than ammonia in the reaction with nickel chloride. For example, diethanolamine, triethanolamine, pyridine or morpholine are sufficiently basic so that a similar brown pigment was obtained.

EXAMPLE 8.

Alpha-naphthylamine (143 parts) was diazotised in the usual way with 250 parts of 10 Normal hydrochloric acid and 200 parts of 5 Normal sodium nitrite. The filtered solution was added to a solution composed of 200 parts of 2-hydroxy-3-naphthoic acid dissolved in 4000 parts of water containing 42 parts of sodium hydroxide and 159 parts of sodium carbonate. The insoluble monoazo colour was filtered and washed. The filter cake was slurried in 3000 parts water. To this suspension was added 262 parts of nickel chloride ($NiCl_2.6H_2O$) and 93 parts of aniline. The mixture was then heated to 90° C. and held at this temperature for 3 hours. The pigment was then filtered, washed and dried. The dried pigment was rubbed into a lithographic varnish, resulting in a black ink having a violet tint. The fastness to light was very good.

The same pigment was obtained by using in place of 93 parts of aniline, an equivalent molecular proportion of phenyl ethanolamine or phenyl diethanolamine or 120 parts urea or 500 parts of aqueous ammonium hydroxide of sp. gr. 0.880 as the acid acceptor.

The following table shows the results obtained by using other diazo components than para-nitro-aniline, coupling with 2-hydroxy-3-naphthoic acid and then metallising with the metal indicated and in the manner described in the foregoing Examples. The properties of these pigments are similar to those heretofore described except where it is otherwise noted.

Example	Diazo Component	Metal	Colour of Textile Print
9	Aniline	Cobalt	Red Brown
10	para-Chlor-aniline	,,	,, ,,
11	,, ,,	Nickel	,, ,,
12	meta- ,,	,,	,, ,,
13	meta-Nitroaniline	Cobalt	,, ,,
14	3-Nitro-4-chlor-aniline	,,	,, ,,
15	,, ,, ,, ,,	Nickel	,, ,,
16	2-Chlor-4-nitro-aniline	Cobalt	,, ,,
17	,, ,, ,, ,,	Nickel	,, ,,
18	2-Nitro-4-amino-toluene	Cobalt	Brown
19	,, ,, ,, ,,	Nickel	Red Brown
20	2-Amino-5-nitro-toluene	Cobalt	,, ,,
21	,, ,, ,, ,,	Nickel	,, ,,
22	*o*-Anisidine	,,	Maroon
23	*p*-Anisidine	,,	Brown
24	2-Amino-4-nitro-anisole	Cobalt	Bordeaux
25	,, ,, ,, ,,	Nickel	,, (redder)
26	2-Amino-5-nitro-anisole	Cobalt	,,
27	,, ,, ,, ,,	Nickel	Violet
28	3-Chlor-4-ethoxy-aniline	Cobalt	Bordeaux
29	,, ,, ,, ,,	Nickel	,,
30	4-Amino-4'-ethoxy-diphenylamine	Cobalt	Blue
31	,, ,, ,, ,,	Nickel	,,
32	alpha-Naphthylamine	Cobalt	,,
33	beta-Naphthylamine	,,	Brown
34	,, ,,	Nickel	Bordeaux
35	alpha-Amino-anthraquinone	Cobalt	Red Brown
36	,, ,,	Nickel	,, ,,

Examples of other suitable diazo components are ortho-, meta- and para-toluidine; 1:3-dimethyl-4-aminobenzene and para-xylidine; ortho-chlor-aniline, ortho-, meta- and para-bromo aniline; chloro-toluidines; meta-anisidine; ortho-, meta- and para-phenetidines; chloro-anisidines, other chloro-phenetidines, 2:5-dimethoxyaniline, other nitro-chlor-anilines; other nitro-anisidines; nitro-phenetidines; meta-amino-benzotrifluoride; other dichlor-anilines; trichlor-anilines, other nitro-toluidines; nitro-chlor-toluidines; benzoyl-meta- and para-phenylene-diamine; meta- and para-aminoacetophenone; meta- and para-aminobenzophenone; ortho-, meta- and para-amino-phenyl-alkyl sulphones; para-dodecyl-aniline; ortho-, meta- and para-amino-benzene-sulphon-dimethyl-amides; ortho-, meta- and para-cyano-aniline; ortho-, meta- and para-amino alkyl

benzoates; ortho-, meta- and para-amino-diphenyl - ether; 4 - nitro - 4' - amino-diphenyl - sulphide; 4-amino-diphenyl-amine; 4 - amino - 4' - ethoxy - diphenyl-amine; 2- and 4-amino-diphenyl; 2-amino-benzothiazole; 2-amino-6-ethoxy-benzo-thiazol; 2-amino-4-methyl-thiazol; 5-, 6- and 8 - amino - quinoline; 1-phenyl-3-methyl-4-amino-5-chlorpyrazol.

The metallisation does not go to completion in the presence of free mineral acids. A sufficient amount of an alkaline compound must be available in the medium as an acid acceptor to combine with the free acid as it is liberated from the metal salt where that is a salt of a mineral acid and as the metallisation proceeds. The pH value of the metallisation medium should be greater than about 6.5. The term "acid acceptor" in the specification and claims refers to an alkaline compound which is added to the metallisation medium to maintain a pH value greater than 6.5 and which will combine with the free mineral acid as it is liberated during metallisation. Any alkaline substance which functions in the manner indicated can be used instead of the acid acceptors heretofore specifically mentioned. Illustrations of such other compounds are propylamine, mono-, di- and tri-methylamine, ethylamine, formamide, acetamide, dimethyl formamide, hexylamine, cyclohexylamine, methyl glucamine, taurine, beta-dimethyl amino propanol sulphonic acid (Chemical Abstracts, 1937, *31*, 6615), toluidines, xylidines, naphthylamines, diphenylamine, piperazine, dimethyl sulphanilic acid, melamine, pyrrole, indole, carbazole, hexamethyleneimine, hexamethylene tetramine, mono- and dimethyl glycine, dimethylol urea, sodium formate, and sodium oxalate, potassium glycollate, potassium gluconate, potassium tartrate, sodium citrate, sodium maleate, sodium succinate and sodium chloracetate. Some of these basic compounds coordinate with the metal complex in the manner similar to that in which ammonia coordinates with the compound described in Example 1. This coordination depends to a large extent on the basic compound used and upon particular conditions present in the process of treatment.

In the metallising operation, the mixture is always alkaline, preferably having a pH value of about 7 to 10, and the salt of the metallising metal may be present in the molecular proportion which is needed as indicated by the formula given herein for the compounds, but a moderate excess, say about 10% of the salt over the amount indicated by theory, is desirable.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. Process for the manufacture of new monoazo pigments comprising coupling with 2-hydroxy-3-naphthoic acid, which may be optionally substituted on the ring not containing the hydroxy group with halogen, nitro-alkyl or alkoxy groups, a diazotised arylamine which is devoid of hydroxy groups ortho to the sole diazotisable amino group and which is devoid of carboxy groups and sulphonic acid groups, and then treating with an agent yielding metal to form a nickeliferous or cobaltiferous metal complex which contains two metal atoms per two molecules of the monoazo combination, at least one of the metal atoms being nickel or cobalt and the other metal atom being from a group consisting of metals having an atomic weight of 54 to 65, and the alkaline earth metals, such as copper, nickel, cobalt, iron manganese, calcium, barium and strontium.

2. Process for the manufacture of new monoazo pigments substantially as described with reference to the foregoing Examples.

3. New monoazo pigments whenever manufactured by a process claimed in either of the preceding Claims or by an obvious chemical equivalent thereof.

Dated the 5th day of June, 1944.

J. W. RIDSDALE,
Solicitor for the Applicants.

Leamington Spa: Printed for His Majesty's Stationery Office, by the Courier Press.—1945.